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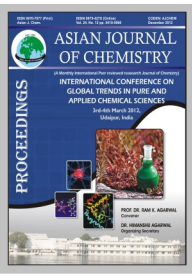

Adsorptive Removal of Metanyl Yellow on Mesoporous Nickel Aluminophosphate Molecular Sieves from Aqueous Solution†

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Metanyl yellow, an anionic dye, toxic to the environment by polluting the water bodies has removed from aqueous solution through adsorption method over mesoporous nickel aluminophosphate (Ni-$AlPO_4$). Attempts have been made through batch removal of the dye and the adsorbent has been found to exhibit good efficiency to adsorb metanyl yellow. Under batch technique, the effect of contact time, temperature, concentration and dosage of adsorbent have been studied to find out the maximum uptake of dye on adsorbent. The dye uptake on the adsorbent is found to follow Langmuir and Freundlich adsorption isotherms models and a second order rate kinetics. Adsorption of metanyl yellow on Ni-$AlPO_4$ is influenced by the temperature. The adsorption thermodynamic parameters, namely ΔH°, ΔG° and ΔS°, have determined for the adsorption. The ΔH° value proved that the adsorption process is endothermic. The positive ΔS° value indicates that entropy is a driving force for the adsorption. The negative ΔG° value shows the adsorption process is spontaneous.

Key Words: Dye removal, Aluminophosphate, Mesoporous molecularsieves, Metanyl yellow, Adsorption kinetics, Adsorption isotherms, Adsorption thermodynamics.

INTRODUCTION

Dyeing and dye manufacturing industries released 15 % of the total world production of dyes is lost during the dyeing process[1]. They consume large volumes of water and chemicals and generate dye effluent in large volumes. Colour is one of the greatest contaminants in wastewater, as it is highly visible and undesirable even though at low concentration. Colour contamination causes considerable environmental pollution because it absorbs and reflects sunlight entering the water, which interferes with the growth of bacteria, impedes photosynthesis in aquatic plants[2]. In order to solve this problem, different physical and chemical processes of colour removal have been investigated, such as coagulation, flocculation, biosorption, photodecomposition and ultrafiltration[3-6]. The developed adsorption method for the removal of metanyl yellow from wastewater has been found easy, versatile and economic because of easy operation, simple design and less investment[7]. The adsorbents were now utilized to assess their proficiency for the removal of toxic dye metanyl yellow. Various researchers have utilized adsorption technique for the removal of toxic dyes from wastewater by using various adsorbents like Aminofunctionalized acrylamide-maleic acid hydrogels[8], bottom ash, deoiled-soya[9], Fe-zeolitic tuff[10], Brazil nut shells[11] cross-linked chitosan[12].

In the present investigations the removal of metanyl yellow on mesoporous Ni-$AlPO_4$ is studied by the batch adsorption technique under the conditions like contact time, dye concentration and temperature.

EXPERIMENTAL

In the synthesis of Ni-$AlPO_4$, aluminium hydroxide was added to the solution of sodium dodecylbenzenesulfonate with vigorous stirring. Then phosphoric acid solution was added to the mixture. The mixture was stirred for 6 h at room temperature. The final gel, with a molar composition is $0.8Al_2O_3$:P_2O_5:0.5SDBS:0.2NiO:$300H_2O$. The gel was heated at 150 ºC with stirring up to the complete precipitation of the mesoporous nickel aluminophosphate molecular sieves. The final product was collected by washed repeatedly with distilled water, filtered, dried and calcined at 600 ºC for 3 h.

The synthesized mesoporous Ni-$AlPO_4$ sample was characterized by the following analytical techniques. The Fourier-transform infrared (FT-IR) measurement of sample was recorded by JASCO FT-IR model Spectrophotometer. Nitrogen adsorption-desorption measurement were made using on Micromeritics, ASAP 2020 V3.00 H at 77 K. The surface area of the sample was obtained by the BET method and the pore size distribution was calculated from the adsorption

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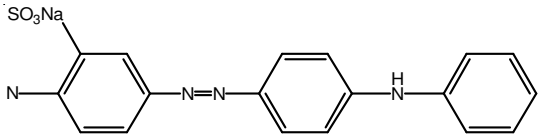
branch of the isotherm based on BJH method. A double beam UV/VIS spectrophotometer (Perkin Elmer, Lambda 25) was used to determine the concentration of dye samples. The calcined Ni-$AlPO_4$ was used to remove the metanyl yellow dye (**Scheme-I**) from aqueous solution.



Scheme-I: Structure of metanyl yellow dye

Adsorption isotherm studies: The distribution of metanyl yellow between the adsorbent and solution is determined by Langmuir and Freundlich isotherms.

Adsorption isotherm data at different concentrations are measured for the adsorption of metanyl yellow and fitted with Langmuir adsorption isotherm equation. This study has been carried out as a model for understanding the monolayer adsorption of metanyl yellow on Ni-$AlPO_4$. The Langmuir equation is represented as

$$\frac{C_0}{C_e} = \frac{1}{Q_{max}K_L} + \frac{C_e}{Q_{max}} \quad (1)$$

where, Q_e is the equilibrium concentration of dyes on the adsorbent (mg g^{-1}), C_e is the equilibrium concentration of dyes in solution (mg L^{-1}), Q_{max} is the monolayer capacity of adsorbent and K_L is the Langmuir adsorption constant. The Langmuir constant K_L is a measure of the affinity between adsorbate and adsorbent and $1/K_L$ value gives half maximum adsorption. Plot of C_e/Q_e *vs*. C_e is a straight line with slope $1/Q_{max}$ and intercept $1/Q_{max}K_L$.

Freundlich adsorption isotherm: The adsorption studies are carried out at various concentrations for metanyl yellow and the adsorption values are applied to the Freundlich equation. This study has been carried out as a model for understanding the multilayer adsorption of metanyl yellow on Ni-$AlPO_4$. The Freundlich equation is represented as:

$$\ln Q_e = \ln K_F + (1/n) \ln C_e \quad (2)$$

where, K_F and 1/n are the Freundlich constants. The plot of ln Q_e *vs*. ln C_e gave a straight line with the intercept K_F and the slope 1/n.

RESULTS AND DISCUSSION

Fig. 1 shows Fourier transformer infrared of the as-synthesized, calcined and thermally treated at 1173 K Ni-$AlPO_4$ samples. The Fig. 1(a) shows that the strong and broad band in the range of 3400-3200 cm^{-1} is assigned to the O-H vibration of crystalline water that exists in the as-synthesized sample. The complete removal of the surfactant is confirmed by the fact that the FT-IR spectroscopy shows that the characteristic C-H valence bands at 2930-2900 cm^{-1} as well as C-H deformation band around 1460 cm^{-1} is absent after calcination at 600 ºC [Fig. 1 (b and c)].

Nitrogen adsorption-desorption measurement: Fig. 2 shows a typical nitrogen adsorption-desorption isotherms of the mesoporous Ni-$AlPO_4$ synthesized by SDBS template. The isotherm is of type IV as typical of mesoporous materials. N_2 adsorption at low relative pressure ($P/P_0 < 0.3$) is accounted for monolayer adsorption of N_2 on the walls of the mesopores. The pore size distribution (diameter) has its maximum at 35.4 nm and the mesoporous $AlPO_4$ has the surface area 94.6 m^2/g.

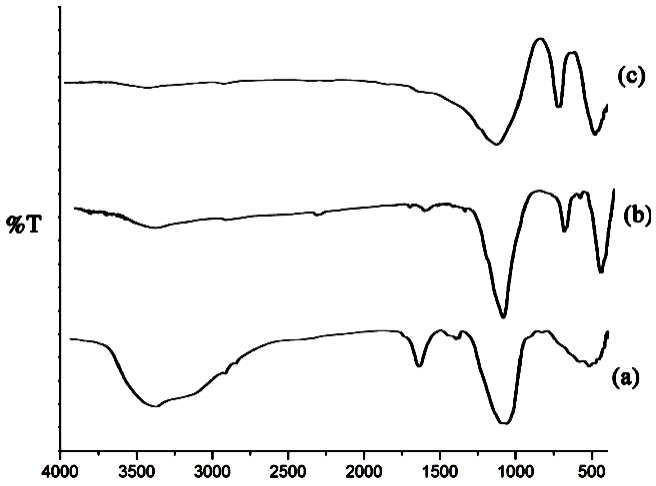


Fig. 1. FT-IR spectrum of a) assynthesized; b) calcined; c) thermally treated at 1000 ºC mesoporous Ni-$AlPO_4$

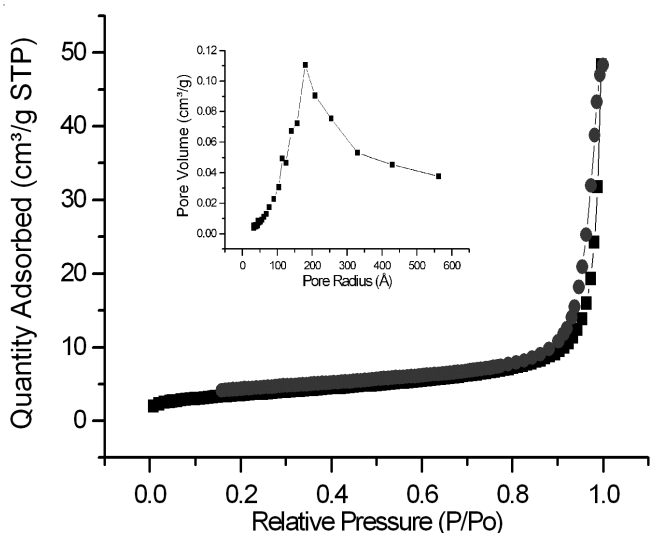


Fig. 2. (a) N_2 sorption isotherms and (b) corresponding pore size distribution of calcined mesoporous Ni-$AlPO_4$

Adsorption studies: adsorption kinetics: The maximum adsorption equilibrium is observed at 3 h for metanyl yellow on Ni-$AlPO_4$. The adsorption kinetics shows the progress of the adsorption capacity through time and it is necessary to identify the types of adsorption mechanism in a given system. The experimental values are introduced in the pseudo second order kinetics equation for calculating rate constant. The equation is

$$t/Qt = 1/ kQ^2e + 1/Qet \quad (3)$$

where, k is the rate constant, Q_e and Q_t are the amount of dye adsorbed per unit mass of the adsorbent at equilibrium and t is time. The plot of t/Q_t *vs*. t gives straight line. Linear plots of the t/Q_t *vs*. t is given in the Fig. 3. The linear regression coefficient higher than 0.99 indicated that the kinetic equation obeys the pseudo-second order adsorption process of metanyl yellow

on Ni-$AlPO_4$. Langmuir and Freundlich adsorption isotherm parameters are given in Table-1. The kinetic parameters are shown in Table-2.

TABLE-1
LANGMUIR AND FREUNDLICH ADSORPTION ISOTHERM PARAMETERS

Langmuir isotherm parameters		Freundlich isotherm Parameters	
Q_{max}(mg/g)	17.37	1/n	0.266
K_L	0.074	K_F	4.03
R^2	0.986	R^2	0.826

TABLE-2
KINETICS PARAMETERS FOR THE ADSORPTION OF METANYL YELLOW ON Ni-$AlPO_4$

Kinetic parameters	Values
K	0.003
Q_e	9.46
R^2	0.995

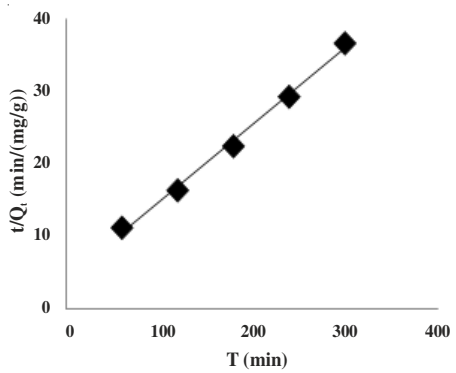


Fig. 3. Pseudo second order kinetic plot for adsorption of metanyl yellow on mesoporous Ni-$AlPO_4$

Adsorption isotherms: The adsorption isotherms Langmuir and Freundlich (Figs. 4 and 5) show that the dye adsorption capacity of Ni-$AlPO_4$ increased with initial dye concentration until saturation. Results obtained from the adsorption isotherm were evaluated by means of the Langmuir and Freundlich adsorption models. In the Langmuir model, it is assumed that a dye monolayer is formed on a relatively regular Ni-$AlPO_4$ surface and the adsorbed amount of molecules depends on the equilibrium concentration of adsorbed molecules according to the eqn. 1. It is seen that the Langmuir isotherm model gave the good result for metanyl yellow (regression coefficient R^2 is 0.986).

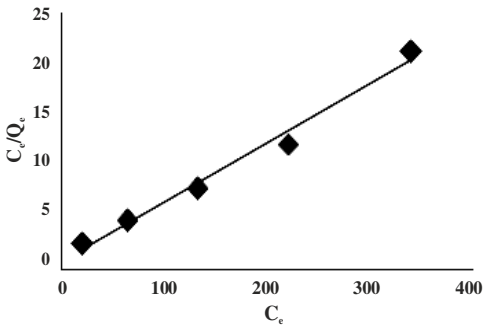


Fig. 4. Langmuir adsorption isotherm plot for adsorption of metanyl yellow on mesoporous Ni-$AlPO_4$

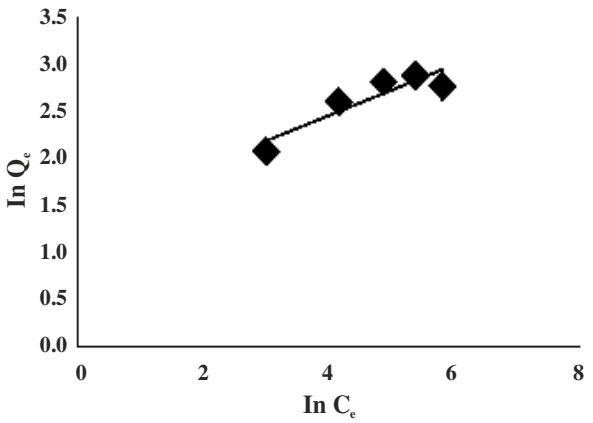


Fig. 5. Freundlich adsorption isotherm plot for adsorption of metanyl yellow on mesoporous Ni-$AlPO_4$

Adsorption thermodynamics: The thermodynamic parameters, namely free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) have an important role to determine spontaneity and heat change for the adsorption process. The thermodynamic parameters are calculated using the following relations.

$$\Delta G^o = -RT \ln K_D \quad (4)$$

$$\ln K_D = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (5)$$

where; K_D is the distribution coefficient of the adsorbate, q_e and C_e are the equilibrium concentration of metanyl yellow on Ni-$AlPO_4$ (mg g^{-1}) and in the solution (mg L^{-1}), respectively. R is the universal gas constant (8.314 J/mol K) and T is the temperature (K). ΔH^o and ΔS^o parameters can be calculated from the slope and intercept of the plot ln K_D *vs.* 1/T, respectively (Fig. 6). From eqn. (4), ΔG^o is calculated for different temperatures. Results are summarized in Table-3. The thermodynamic studies reveals that the adsorption of metanyl yellow on Ni-$AlPO_4$ is endothermic and the adsorption is chemisorptions (ΔH^o > 40 KJ/mol). The negative value of free energy (ΔG^o) change indicates that the process is spontaneous. The positive values of entropy (ΔS^o) were obtained in case of metanyl yellow on Ni-$AlPO_4$, indicating the increased randomness at the solid-solution interface during the fixation of metanyl yellow on the active sites of the Ni-$AlPO_4$.

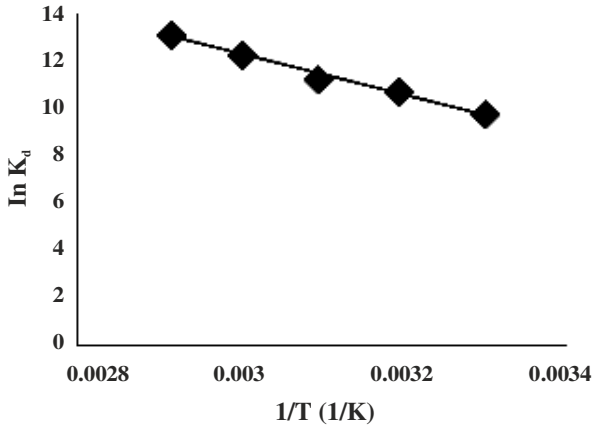


Fig. 6. Thermodynamic plot for adsorption of metanyl yellow on mesoporous Ni-$AlPO_4$

TABLE-3
THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF METANYL YELLOW ON Ni-$AlPO_4$

Thermodynamic parameters	Values
ΔH^o (KJ/mol)	70.846
ΔS^o (J/mol K)	314.7
ΔG^o (KJ/mol)	
T=303 K	-24.636
T=313 K	-27.932
T=323 K	-30.188
T=333 K	-33.964
T=343K	-37.414

Conclusion

This study investigates that the Ni-$AlPO_4$ is an adsorbent for the removal of metanyl yellow from aqueous solution. Higher percentage of metanyl yellow removal by Ni-$AlPO_4$ is possible provided that the initial concentration of the dye solution is 100 mg/L. The equilibrium between the adsorbate in the solution and on the adsorbent surface is practically achieved in 3 h. Adsorption kinetics is found to follow pseudo second-order rate equation. Equilibrium adsorption data for metanyl yellow on Ni-$AlPO_4$ are well represented by the Langmuir and Freundlich isotherm models. This study concludes that adsorption of metanyl yellow on Ni-$AlPO_4$ is spontaneous.

REFERENCES

1. H. Zollinger, Colour Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments, 2nd Revised ed. VCH, New York, (1991).
2. R. Sanghi and B. Bhattacharya, *Color. Technol*., **118**, 256 (2002).
3. S. Babel and T.A. Kurniawan, *J. Hazard. Mater.*, **97**, 219 (2003).
4. C. Galindo, P. Jacques and A. Kalt, *J. Photochem. Photobiol. A,* **130**, 35 (2000).
5. T. Robinson, G. McMullan, R. Marchant and P. Nigam, *Bioresour. Technol.*, **77**, 247 (2001).
6. Y. Fu and T. Viraraghavan, *Bioresour. Technol.*, **79**, 251 (2001).
7. A. Dabrowski, *Adv. Colloid. Int. Sci.*, **93**, 135 (2001).
8. H. Kasgoz, *Colloids Surf. A*, **266**, 44 (2005).
9. A. Mittal, J. Mittal and L. Kurup, *J. Hazard. Mater.*, **B137**, 591 (2006).
10. E. Gutierrez-Seguraa, M. Solache-Riosb and A. Colin-Cruza, *J. Hazard. Mater.*, **170**, 1227 (2009).
11. S.M. de Oliveira Brito, H.M.C. Andrade, L.F. Soares and R.P. de Azevedo, *J. Hazard. Mater.*, **174**, 84 (2010).
12. R.C. Antonio, F.S.V. Eunice, M.G.T. Andrea and E.B. Roy, *J. Hazard. Mater.*, **153**, 566 (2008).